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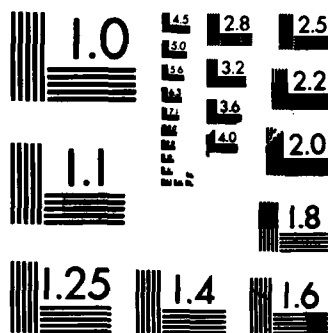
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Technical Report No. 3

**INORGANIC POLYMERS**

Proceedings of Conference on  
Integration of Fundamental Polymer Science and Technology,  
Rolduc II, April '87, Limburg, Netherlands  
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by

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19. Abstract (Continued)

The purpose of this paper is to select and discuss polymers primarily from these two inorganic classes and to highlight some aspects of their thermal stability, toxicity (or lack of), morphology and structure-property relationships that are challenging academically and developing industrially in our time. ←

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## INORGANIC POLYMERS

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### ABSTRACT

Inorganic polymers were first synthesised during the latter part of the last century, but commercial development was slow initially. The polysiloxanes have been exploited successfully since the late 1940's. Amongst other uses they are now being developed as precursors for silicon nitrides and silicon carbides in high temperature applications. More recently polyphosphazenes, a rapidly growing new class of polymers since the mid 1960's, have received much attention. These polymers represent the first important new class of semi-inorganic plastics since the siloxanes. They have great potential and may in time prove to be even more useful than the polysiloxanes since many of these materials are also liquid-crystal formers. Besides, a single cyclic monomeric precursor has been used to synthesise a very large number of homo and copolymers whose properties may be varied at will via side group substitution to obtain polymers that are crystalline, elastomeric or foams and thermosets as required. Some of these materials are growing in technological importance despite their cost.

The purpose of this paper is to select and discuss polymers primarily from these two inorganic classes and to highlight some aspects of their thermal stability, toxicity (or lack of), morphology and structure-property relationships that are challenging academically and developing industrially in our time.

## INTRODUCTION

High polymers with inorganic elements comprise an important and growing field of macromolecules that have considerable molecular diversity [1,2]. Many of these materials are academically challenging and industrially useful too. Not only do they exhibit varied and interesting physical properties, but their usefulness has been established [3,4] in many cases. At the present time these newer classes of materials appear to have unparalleled potential particularly in the realm of polyphosphazenes where in enormous variety of chemical structures may be developed from a single cyclic monomer, now rivals most generic organic macromolecules. Although the polysiloxanes have been well established since the 1940's [5,6], new syntheses as well as developments and improvements are growing much less rapidly than in the polyphosphazenes. Of course polymers with such as Al, S, N, Ti, Sn, Ge and other inorganic elements have been introduced into macromolecular backbones over the past decades. Most of the salient features of these systems have been mentioned in texts [7] and recent literature [8]. Still, much more remains to be investigated even though every branch of industry and society has been a benefactor of the current "plastics age" in some form or other in this century.

The synthesis of polysiloxanes and polyphosphazenes especially has received much attention since the 1960's [9-11]. Likewise, molecular, thermal and mechanical stability, specific solvent resistance, biomedical qualities and useful engineering material parameters, toxicological, corrosion and fire resistance characteristics place many of the inorganic polymers "second to none" amongst other synthetic polymers in the world today. However this is not all, for many polysiloxanes and polyphosphazenes exhibit qualities which place them in a novel category of flexible chain polymers that demonstrate a considerable range of thermotropic or liquid-crystalline-like behavior\* [12]

that is not fully understood yet. This behavior is further complicated by the fact that several polymorphs are also found in most polyphosphazenes [13].

Inorganic polymers tend to have relatively high temperature properties and are sometimes used as fibrous and stock products. Highly stable fibrous materials have "simple" chemistry as found in silicon carbide and silicon nitride amongst others. Alumina and boron fibers also exhibit high strength and moduli plus a wide range of other appealing properties that qualifies them as unique engineering materials in their own right, or when incorporated in hydrid or heterogeneous systems (notably composites) [7]. They often find special applications in electrotechnics, building, transportation space, textiles, aviation to cite only some examples.

Some remarkable heat resistant systems have been produced through the selective degradation of "macromolecules" [14]. In another well established and important field, several different polymers have been converted successfully to graphite fibers and other geometries too. However, it is worth noting that these appealing materials still fall short of the "polymeric" qualities embodied in graphite (1060 GPa within the layers or sheets) and in diamond around 1200 GPa, which in a sense, sets a goal or upper limit for strong polymeric substances [7].

The physical properties and fundamental characteristics of polysiloxanes and polyphosphazenes especially display considerable diversity. Even though they fall short of these "ideal" or target materials just mentioned, they present a growing challenge to many other commercial materials. This presentation only focusses upon some specific topics on selected inorganic polymers, believed to have far-reaching technological and academic value.

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\*The commonly acknowledged criterion of main chain stiffness appears not to be the only prerequisite for L.C. formation.



Amongst the topics are (i) crystallization kinetics (ii) crystal structure, (iii) interfacial properties and (iv) thermal stability and toxicity of polyphosphazenes.

### Kinetics of Crystallization

Experimentally crystallization of polymers is usually concerned with

(i) bulk transformation rates,

or (ii) spherulitic and/or nucleation rates from the melt.

These techniques monitor the overall development and growth of crystallizing species but they fail to measure changes in lamellar thickness which are fundamental to spherulites and have been well established by electron microscopy [15]. Small angle X-ray scattering (SAXS) and specifically ISSAXS (i.e. in situ SAXS enables lamellar thickness to be measured during spherulitic growth) for both the "primary" and "secondary" phases of development. Two well studied poly(TMPS) fractions [23] of molecular weight fraction (21,000), one of which lies just below the critical value of the melt entanglement molecular weight,  $M_c$ , and the other much higher of 371,000 molecular weight were used. Details and procedures involved in this work have been described recently [16] so that only actual results need concern us here. Both poly(TMPS) fractions exhibited analogous isothermal crystallization behavior, where X-ray scattering intensity increased with time, at constant scattering angle throughout the phase change but the intensity increased as expected with time. After reaching a maximum level, I,

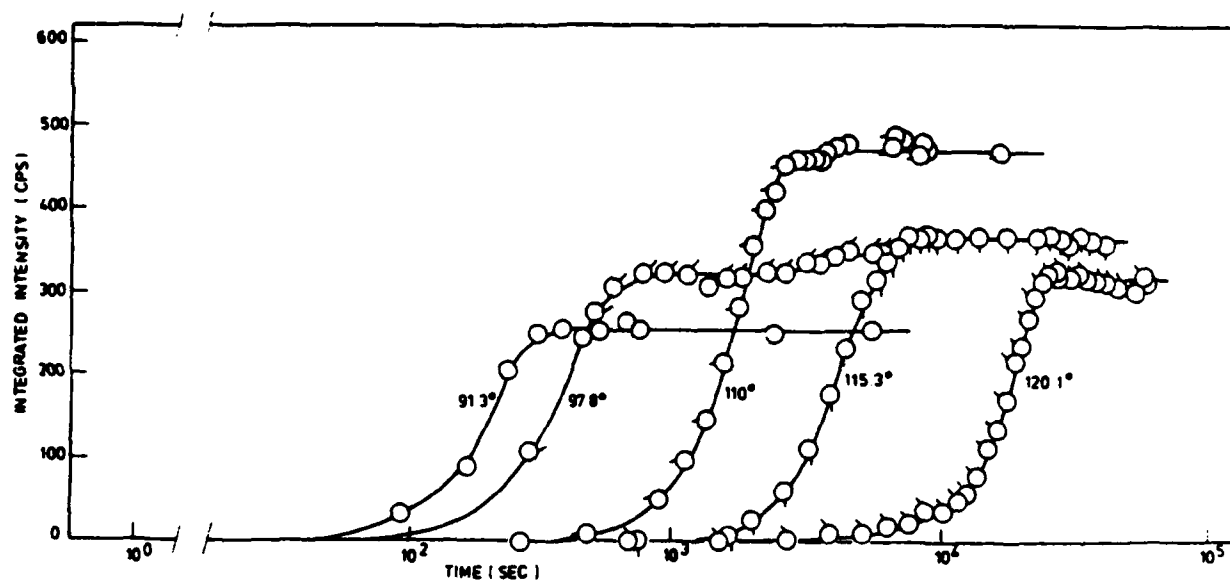


Figure 1(a). Small angle X-ray integrated intensity,  $I$ , vs time (sec) for 371,000 molecular weight fraction of poly (TMPS) at selected isothermal crystallization temperatures.

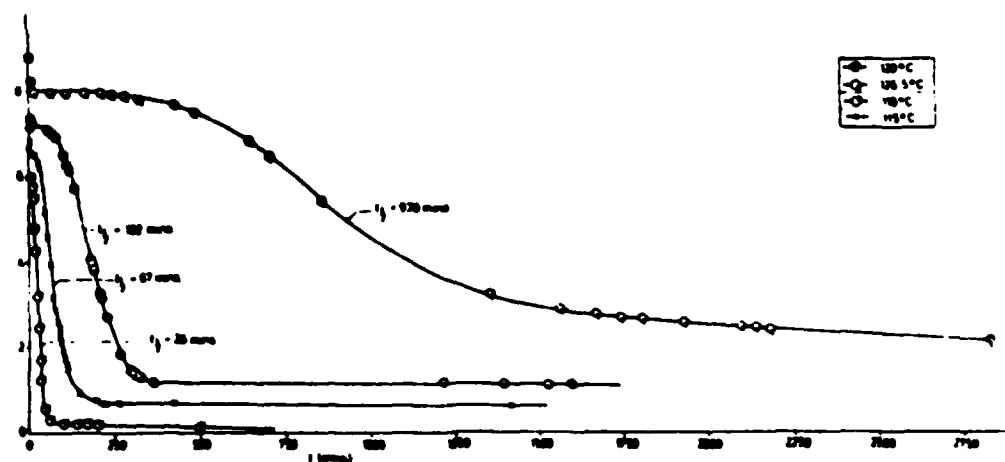


Figure 1(b). Dilatometric isothermal crystallization curve for poly TMPS fraction of molecular weight 37,500 at various temperatures.

did not drop off again precipitously as predicted<sup>†</sup> for a highly transformed crystallizing system by the Guinier equation:

$$I = K \phi (1-\phi) (\rho_c - \rho_a)^2$$

where K is an instrument constant,  $\phi$  is the volume fraction of crystallinity  $\rho_c$  and  $\rho_a$  are the crystalline and amorphous densities respectively for the polymer phases. After crystallization times, well beyond the primary transformation stage, I remained almost invariant and the typical secondary transformation observed in the 371,000 fractions<sup>\*</sup> was absent (see Figure 1(a)) whereas dilatometry result indicated clearly its existence, even in fractions one order of magnitude lower in molecular weight (see Figure 1(b)). Anyhow, other X-ray results for ISSAXS and ISWAXS using synchrotron radiation [17] exhibit I vs t curves where I is virtually constant. This will be discussed later in the case of polyphosphazenes. The invariance of the crystallite size with time and the relatively good agreement (Figure 2) between  $t_{1/2}$  values for primary crystallization lends confidence to the ISSAXS technique. The secondary or "after" crystallization although not exclusive to dilatometry, is usually noted for bulk transformation studies only. Its origin is not proven, but it has been attributed to some form of inter- and intraspherulite growth which occurs slowly, over long times.

Other interesting ISSAXS observations showed that there was a substantial difference in the long period obtained at comparable undercooling for the low and high poly(TMPS) fractions[16]. It seems that "trapped" entanglements or

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<sup>†</sup>Lately modified<sup>(1)</sup> to read  $I = K V_s \phi (1-\phi) (\rho_c - \rho_a)^2$  where  $V_s$  is the volume fraction of spherulities in the system.

<sup>\*</sup>Low molecular weight poly(TMPS) fraction (21,000 included) do not exhibit secondary crystallization even by dilatometry.[ ]

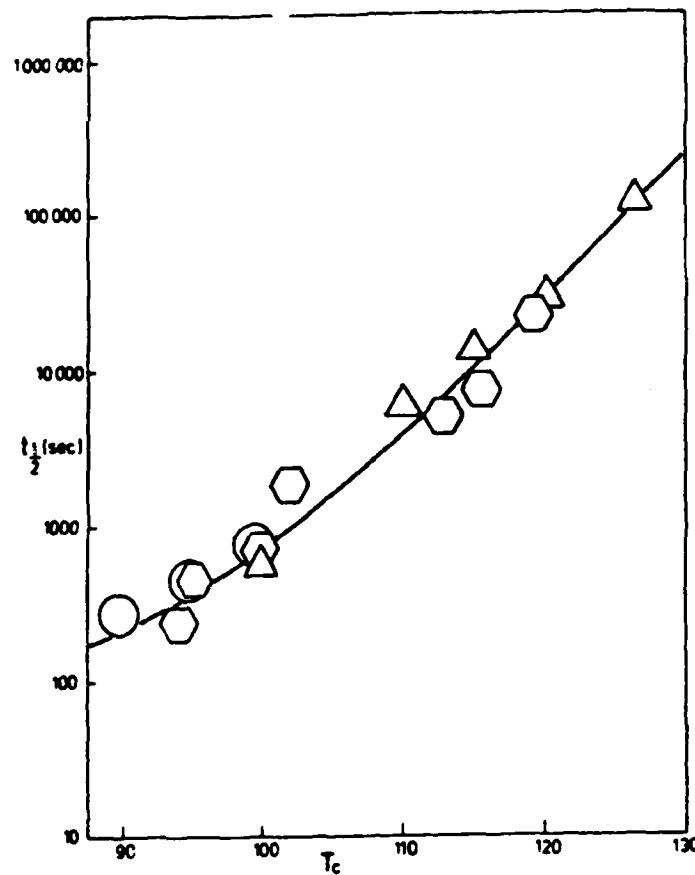


Figure 2. Half time values,  $t_{1/2}$ , from in situ SAXS and other techniques plotted as a function of crystallization temperature for 21,000 poly (TMPS) fraction.

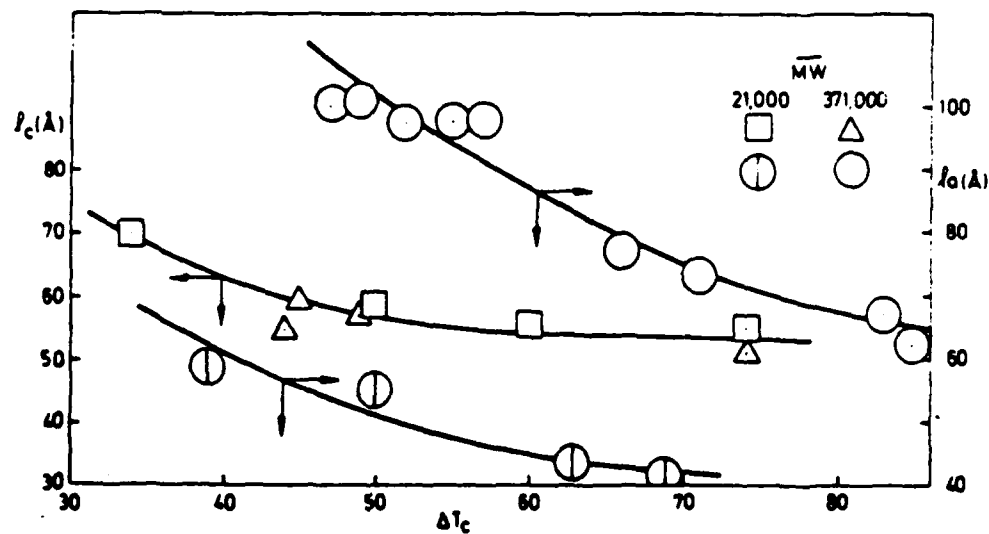


Figure 3. Crystallite dimensions,  $l_c$  (Å) and interfacial dimension,  $l_a$  (Å) as a function of undercooling for 21,000 and 371,000 poly (TMPS) molecular weight fractions (reproduced by permission).

tie-molecules involved in primary isothermal crystallization function as a controlling factor in major sample morphology and mechanical properties too. Note that spherulitic growth [18], primary associated with the melt-solid interface is essentially invariant for high molecular weights well above,  $M_c$ , where intermolecular effects dominate properties. Changes in crystallinity with molecular weight clearly indicate the primary influence of chain length on morphology and properties [19]. The SAXS period is much larger for the higher molecular weight sample at corresponding undercooling. Besides, the SAXS spacing of the 371,000 sample "shrinks" substantially upon cooling the sample below the crystallization temperature,  $T_c$ , to room temperature, sometimes. For example the 371,000 decreases from 166Å to 114Å on going from 121.2° to 40°C whereas for the 21,000 specimen it only alters from 118Å to 90Å over almost the same span of undercooling. This difference represents a smaller incremental change to be identified with a smaller intercrystallite layer spacing in the latter sample. Interestingly this behavioral pattern which is reversible, contrasts sharply with heating crystallized specimens from room temperature up to  $T_c$  and then cooling again, when irreversible crystallite thickening was always noted for poly(TMPS) [20].

One of the most important conclusions from this isothermal SAXS work is that  $l_g$  shows a strong function of molecular weight (see Figure 3). Folding dominates in most crystallization processes but it becomes less perfect as the molecular weights increases thus giving rise to larger "disordered" interfaces\*. This trend has already been substantiated for poly(TMPS)

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\*Extensive results on melt crystallized polyethylene fractions characterized by electron microscopy are in accord with this picture. I.G. Voigt - Martin and L. Mandelkern, J. Polym. Sci. (Poly. Phys. Ed.) 1984, 22, 1901 and earlier papers.

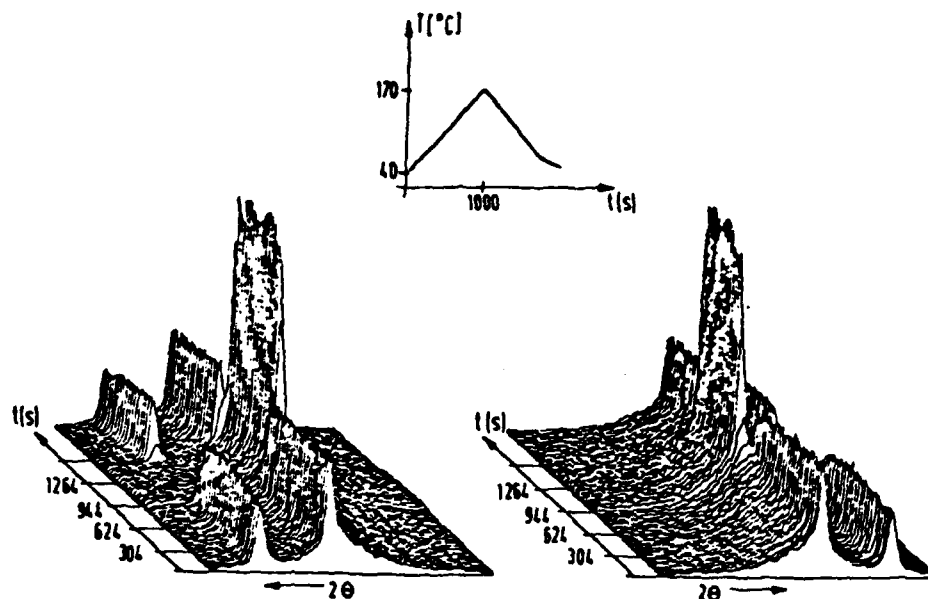


Figure 4. Changes in situ WAXS (8 sec) spectra with ramp heating and cooling through the  $T(1)$  transition for PBMPP.

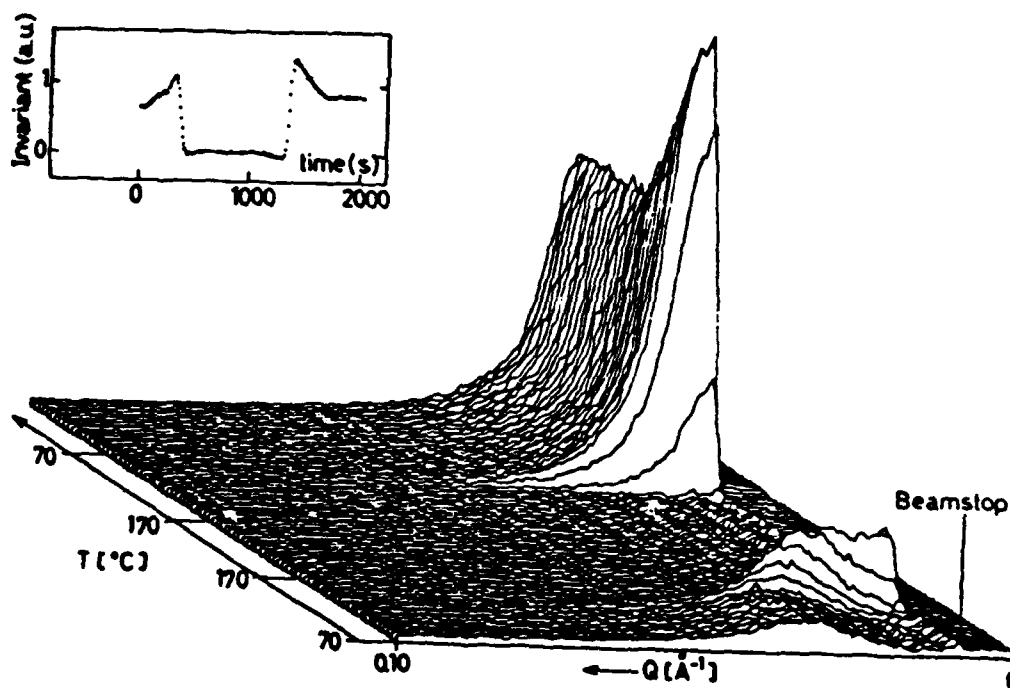


Figure 5. Selected 8 sec in situ SAXS spectra recorded during ramp heating and cooling of PBMPP. These difference spectra were obtained by subtracting the scattering at  $170^{\circ}\text{C}$  (i.e. above  $T(1)$ ) to accentuate the small angle peak shift with time and temperature. Changes in the Invariant with time are indicated in the insert.

fractions in this and other publications using bulk [19] and surface characterization techniques [21,22].

Well defined chain folds have already been substantiated for other oligomers\* with chain lengths below the entanglement  $M_c$  in polyethylenes [23,24] and polyethyleneoxides [25] respectively. Since these short chain system hardly qualify as conventional polymers since they do not necessarily interact strongly intermolecularly in the molten state, nor have they non-brittle (tough) mechanical properties.

Now to turn to phase transformation kinetics in polyphosphazenes where thermotropic behavior has been well documented recently [26]. Generally high molecular weight phosphazenes crystallized from dilute solution are not well organized (3D-crystallinity index ~40% level) even though they exhibit a distinct "single" crystal habits [27]. However upon heating these crystals they form a thermotropic (disordered) 2D-phase documented by SAXS and DSC. The phase transformation may be monitored in real time in situ using WAXS and/or SAXS techniques. Figure 4 shows 8 sec. ISWAXS spectra obtained upon heating and cooling a pressed crystal mats of poly[bis(p-methylphenoxy)phosphazene] (PBMPP). Clearly there are improvements in spectral quality and crystallinity measured under these conditions (and quantified by other techniques [28]).

ISSAXS measurements made under similar circumstances, show that the relatively broad SAXS peak of the crystal mat as it moves towards the direct beam, upon ramp heating the sample through  $T(1)$ . An enhanced long period in the vicinity of  $600\text{\AA}$ , which spacing lies on the borderline of the instrumental resolution was obtained (see Figure 5) when this investigation was made. The insert in this figure depicts the changes in the Invariant with time as the

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\*do not have fully developed polymeric properties or physical characteristics.

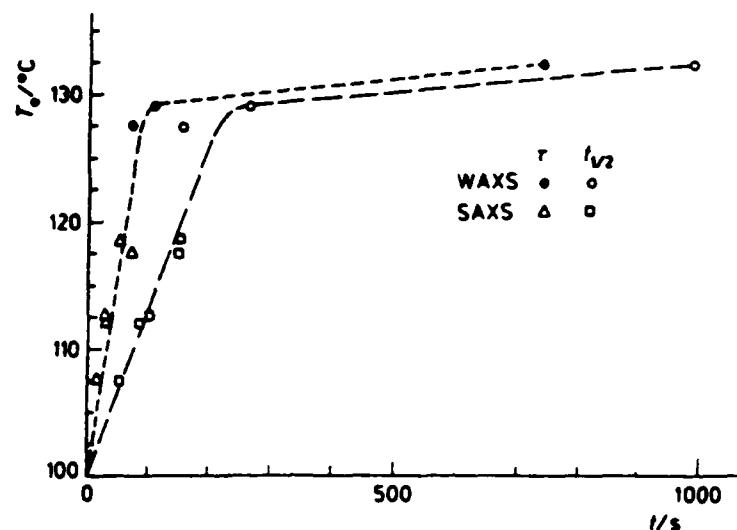


Figure 6. Comparison of induction,  $t$ , and transformation,  $t_{1/2}$  half-times measured by ISWAXS below  $T(1)$  after sample conditioning at  $170^\circ\text{C}$ .

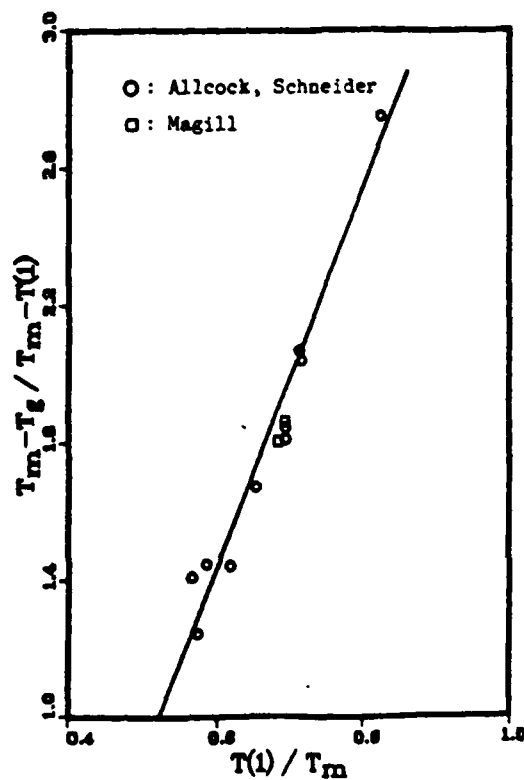


Figure 7. Empirical relationship obtained for thermotropic polyphosphazenes.  $T_g$  and  $T(1)$  are respectively the glass and thermotropic transition temperatures, and  $T_m$  is the final clearing or melting point of the polymer.



T(1) transition is traversed. The spectra in the thermotropic region was subtracted to enhance the SAXS features of pattern. Other work on polyphosphazenes carried out in 1985, appears to be in line with many of the general features portrayed here [29].

As in selected polysiloxanes, it is apropos to compare the kinetics of the 2D to 3D transformation for example in PBMPPP following preconditioning of the sample above T(1) at 170° for 5-15 min. prior to cooling it rapidly (50°/min) to the isothermal transformation temperature,  $T_c$ , below T(1) where the disordered 2D  $\rightarrow$  3D takes place. The transformation embodies a change from a pseudo-hexagonal (2D)  $\delta$ -phase into an orthorhombic 3D,  $\gamma$  phase [17]. The isothermal scattering intensity shows a measurable induction time,  $\tau$ , followed by a rapid rise in intensity during the phase change. At long times the intensity is invariant (ie suggesting that no secondary crystallization is measurable by ISWAXS or ISSAXS). Half-times as a function of "undercooling" ( $T(1)-T_c$ ) are shown in Figure 6. We are now focussing on the amorphous or isotropic  $\rightarrow$  2D transformation where the transformation rate occurs much faster.

The influence of phosphazene side group chemistry on  $T_g$ , T(1) and  $T_m$  parameters fits an empirical relationship\*\* shown in Figure 7. This relationship may be used as a guideline for evaluating the effect of side group substituents on basic physical parameters - i.e. structure-chemistry correlations in thermotropic alkoxy and phenoxyphosphazenes. The magnitude of the [ $T_m - T(1)$ ] range scales with the side chain chemistry, group size and chain flexibility expressed through  $T_g$ .

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\*\*Note that this correlation was reproduced incorrectly elsewhere [31].

#### (ii) CRYSTAL STRUCTURES

Published X-ray structures for polysiloxanes and polyphosphazenes [32,33,34] are few in number and some controversy exists in the case of the latter polymers. Several structures are not cited here. One of the reasons for this seems to obtain from the diversity of polymorphic forms that can coexist in polyphosphazenes. Recently in our laboratory electron and X-ray diffraction investigations been used successfully to demonstrate that there may be three or even four crystal modifications (often including the thermotropic phase) formed in the preparation and heat treatment conditions used for sample preparations. A case in point is illustrated in figure 8 which shows a transition map of 3 crystal modifications and one mesophase in poly[bis(phenoxyphosphazene)]-PBPP. These complications exist in addition to the chemical ones that are encountered in synthesis and molecular weight characterization. For these reasons several complementary methods of specimen characterization are recommended to avoid ambiguities when studying polyphosphazenes.

#### (iii) INTERFACIAL PROPERTIES

Chain folds, however perfectly constructed, constitute defective regions in crystalline homopolymers and copolymers. Their existence has been inferred from morphological and property studies using well characterized short chain polymers. Meticulous crystallization experiments with sharp polyethyleneoxide fractions [23] and long chain n-paraffins [24] support the idea of regular chain folding from the melt\*. However there appears to be accord in principle but not in all details of the morphology of long chain paraffins. The evidence in some other polymers is less convincing at this time. Results (two

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\*Solution crystallization work on polyethylene fractions is not included here for lack of space, although important studies have been published in *Macromolecules*, 1985, 18, 760.



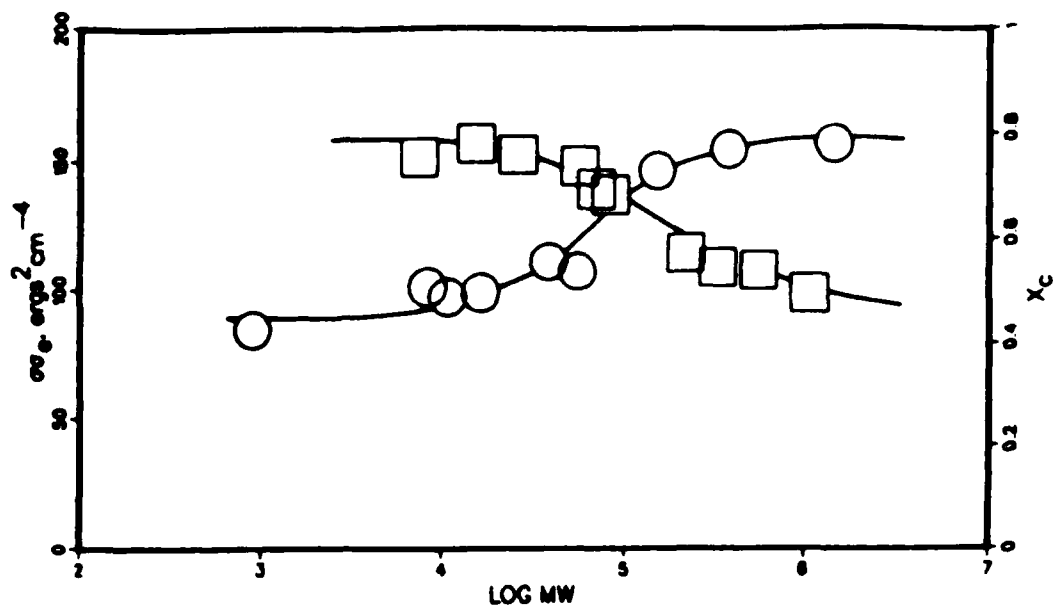


Figure 10. Interfacial surface energy product  $\sigma\sigma_0$  (ergs<sup>2</sup>/cm<sup>4</sup>) from isothermal spherulitic growth rates as a function of molecular weight for poly (TMPS) fractions. Change in crystallinity with chain length is superposed on the same scale.

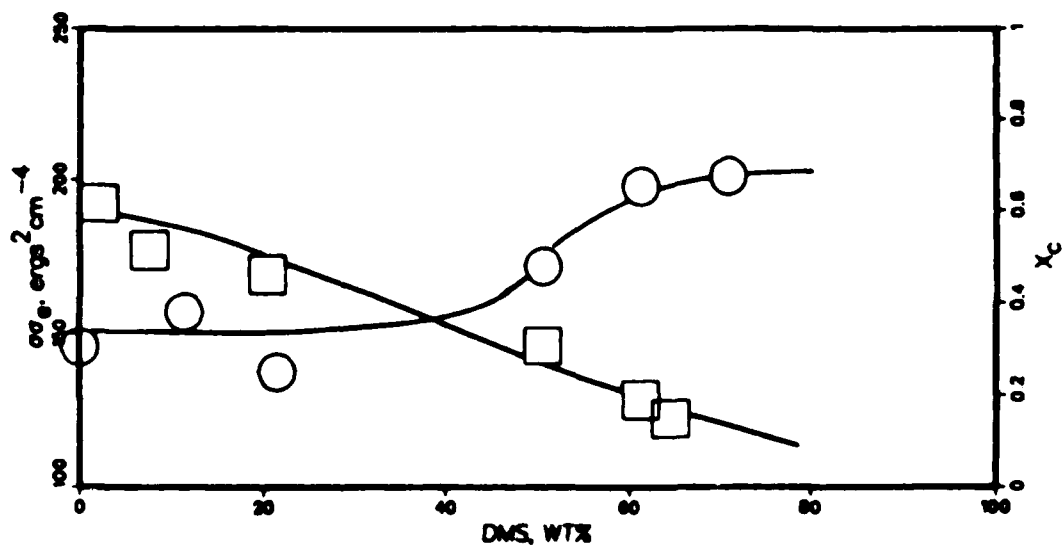


Figure 11(a). In surface energy,  $\sigma\sigma_0$  (erg<sup>2</sup>/cm<sup>4</sup>) determined from isothermal spherulitic growth rates for poly(TMPS)/(DMS) block type copolymers of different compositions (○).

Figure 11(b). Crystallinity from X-ray and DSC measurements as a function of copolymer composition (□).

decades ago) obtained from melt crystallized low molecular weight poly(TMPS) fractions ( $DP < 10$ ) seem to follow this behavior although the fractions used were not well enough defined to permit definitive answers [35]. Anyhow for poly (TMPS) fractions over several orders of magnitude, as molecular chain length increases significantly the regularity of chain folding taking place in solution crystallized samples is measurably reduced, whereas in melt crystallized specimens the surface (or interlamellar regions) exhibit significant perturbations [19]. Imperfect chain folding and lowered crystallinity, is to be associated with trapped entanglements or tie molecules which are more dominant as molecular weight increases [see section (iv)]. Figure 9 clearly shows that crystallinity decreases significantly in melt crystallized polymers of poly(TMPS) and polyethylenes [19(a)]. In keeping with these observations on crystallinity, it was well established years ago that the shorter chain polymers are brittle (however they are crystallized) whereas high molecular weight fractions are invariably tough materials, demonstrating enhanced mechanical behavior is attributable to greater cohesive interactions and more copious tie connections for the stronger higher molecular weight polymers. Evidence from spherulite growth rates [18], although indirect, is evident from Figure 10 where there is an inverse type correlation between interfacial energy, expressed as a product  $\sigma_e$ , ( $\text{ergs}^2/\text{cm}^4$ ) which is determined from isothermal spherulitic growth rates and the corresponding change in crystallinity obtained for the same fractions of poly(TMPS). The decrease in crystallinity index and the simultaneous rise\* in  $\sigma_e$  are to be associated with changes in the interlamellar regions corresponding to enhanced amorphicity. This trend, which now seems to be

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\*This molecular weight dependence of  $\sigma_e$  is not to be confused with changes associated with regime crystallization. All growth is spherulitic.

self-evident and very important from a properties viewpoint, is not considered in the formulation of any of the current kinetic models of crystallization [36]. The fact that there is a significant increase in long-period with chain length in poly(TMPS) fractions [16,19] crystallized from the melt (and to a lesser degree from solution [19] means that the lamellar interface is strongly influenced by the average length of the growing chain as well as the number of nucleation points on a growing lamellar substrate during crystallization. Figure 3 shows that the crystallite regions do not vary much with undercooling under conditions where the overall long-period increases markedly, however the intercrystallite dimensions are altered considerably. There is a significant difference between high (371,000) and low (21,000) molecular weight samples. We will return to this point in the next section.

In block copolymers of poly(TMPS)-(DMS) an analogous but more impressive trend in interfacial characteristics is found. Interfacial energies (obtained again from analysis of spherulitic crystallization) indicate that  $\sigma_e$  increases as a result of interfacial disturbances to be associated with a changing interface due to an accumulation of non-crystallizable DMS material segregated preferentially between crystallizable lamellae (see Figure 11). It is worth recalling that all of the copolymer spherulites appear well defined optically [37] even at highest DMS concentrations (~70wt%) where the overall crystallinity levels (by DSC and X-ray) falls short of 20%. This and other observations indicates that spherulitic textures alone are not a useful indicator of crystallinity even when most of the spherulites are regularly ringed! More striking however is the concomitant decrease in measured crystallinity which occurs whenever the  $\sigma_e$  increases as the DMS component increases. The trend falls in line with the increase in long period (SAXS), measured for these very TMPS/DMS compositions [20].

Elsewhere, it has been clearly established from selective chemical etching measurements [38,39] that the morphology of solution grown crystal surfaces and/or lamellar interfaces (in bulk crystallization), exhibit morphologies that parallel chemical and physical properties in accord with an increasingly perturbed interface as a result of non-crystallizable DMS and some trapped TMPS material between DMS blocks in the copolymers. This results in a fall in crystallinity with increasing DMS volume fraction [21].

#### (iv) SURFACE SPECTROSCOPIC STUDIES

ESCA and FTIR studies for variously prepared poly(TMPS) specimens - namely: (i) solution grown crystal mats, (ii) melt quenched specimens and also (iii) solution cast films of the same molecular weight sample have provided useful insights in polymer surface morphology through chemical etching with dilute HF gas [22]. Carefully prepared samples were supported on cleaned platinum foil and subsequently etched with dry HF/He mixture (10/90 v/v) at 45°C\*. Using X-ray photoelectron spectroscopy, changes in the surface structure with time of etching were followed [22]. DSC and small angle X-ray scattering (SAXS) were also employed to investigate small changes in the bulk characteristics of these etched specimens. Details are already published [22]. The degree of crystallinity was found to increase significantly as the SAXS periodicity decreased with longer etching time. Clearly the crystal surface was removed preferentially by the HF since it was more vulnerable to attack than the more highly resistant crystalline poly(TMPS) core. The trend illustrated in Figure 11 is also in accord with older measurements where HF solution was used as an etchant [21]. These changes in crystallinity

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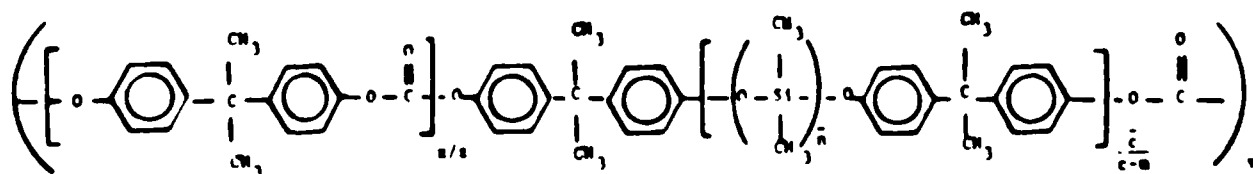
\*It is necessary to conduct these experiments well above the condensation temperature of HF, which lies close to room temperature.

\*Similar definitive experiments have been carried out on nylon single crystals.

determined by DSC, FTIR and ESCA bands all showed that the poly(TMPS) crystals exhibited enhanced crystallinity (80 to 95%) as the vulnerable fold surfaces were etched away. Similarly the (ii) melt crystallized and (iii) solution cast films were found to be more readily degradable by HF than were "single" crystal surfaces, because chemical attack could take place more extensively and longer throughout the many more interlamellar spherulitic regions than on single crystal surfaces. More details of this work are to be found in the literature [22,40].

Recent investigation [40] carried out on unetched poly(TMPS)-(DMS) copolymer crystals also confirms that the non-crystallizable DMS component is segregated to the surface, thus providing direct morphological evidence that is in line with other indirect measurements, using HF solution etching [41]. ESCA and FTIR (ATR) techniques indicate that surface segregated DMS is present in solution grown 90/10 and 80/20 TMPS/DMS crystals. However, crystals containing higher amounts of DMS were comprised of a relatively thick layer of non-crystalline amorphous material in agreement with SAXS measurements for example. Here it has been shown that the substantial increases in long period is to now explained as due to increasing wt% DMS accumulated in these copolymer crystal specimens [41].

Another DMS copolymer is also of interest [42] here since it also provides supporting evidence of surface segregation (speciation) in the polycarbonate -DMS (BPAC/DMS) commercial copolymers (amorphous systems) of chemical structure:-





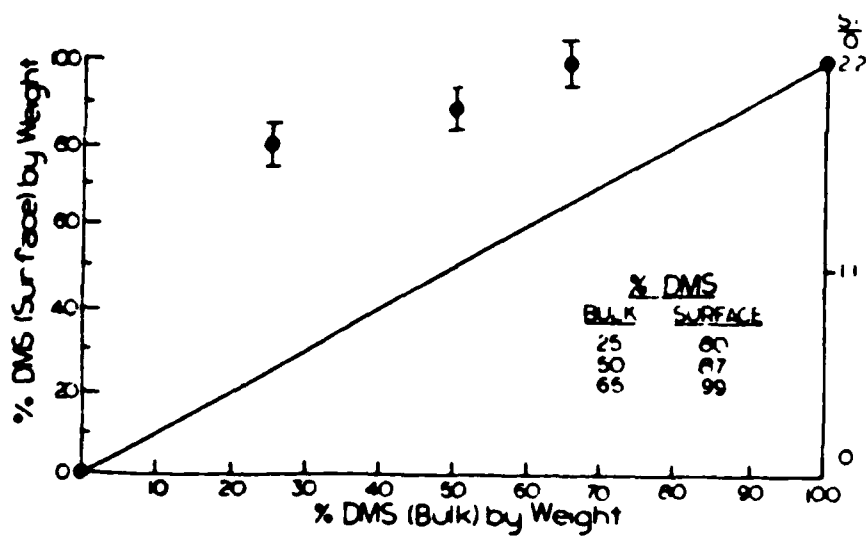


Figure 12(a). Surface composition (wt.% DMS) by ISS versus bulk composition (wt.% DMS).

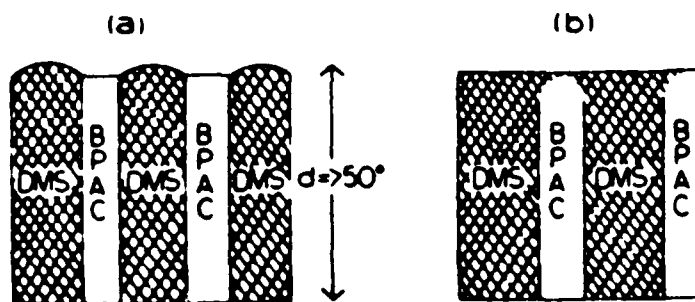


Figure 12(b). Morphological models for BPAC/DMS block copolymers. (i) showing morphology from ESCA measurements and (ii) with their overlayer of DMS only resolvable by ISS techniques.

X-ray photon spectroscopy measurements (ISS) of solution cast samples of this amorphous block copolymer fixed (DMS) shows that the DMS component is surface segregated at all compositions. A simplified morphological model for this system (Figure 12(a)) depicts the DMS surface layer determined by ESCA (range 10-50Å) compared to the more surface sensitive low energy ISS analysis (3-5Å) in depth profiling experiments (see Figure 12(b)). Surface segregation of the "inorganic" DMS occurs over a wide range of polymer compositions, and this is responsible for the surface properties of the polymer, a fact of some importance in some industrial applications.

#### (v) THERMAL STABILITY AND TOXICITY OF POLYPHOSPHAZENES

It is appropriate to digress briefly to some more practical aspects of our past polyphosphazene research. Problems of thermal stability and toxicity of volatile degradation products may be correlated with side chain chemistry. Tests made on a variety of polyphosphazenes as foams, sheets or elastomers (filled and unfilled) indicated that toxicity was reduced considerably if halogenated side groups were avoided as in other polymers. Besides, the mechanism of degradation also proved to be significant and a preliminary behavioral pattern was evident from the samples studied. The char forming ability of selected polyphosphazenes followed a pattern (established here and elsewhere) where char yield in aminoxy-→ phenoxy-→ alkoxy side chain polymers [43]. The latter phosphazene degraded by a chain unzipping reaction (hence very small char residues) whereas phenoxy-materials involved random chain scission with some chain transfer (residues were 20-30% approximately) and the aminoxy provided even larger residues since considerable chain scission occurred with cross-linking occurred in the early stages of degradation [44,45]. Clearly degradation mechanism and volatiles are coupled processes worthy of further inorganic systems including the polysiloxanes

(homo and copolymers) [46]. It seems that properly selected polymer systems should provide considerable fire resistance without the use of fire retardant additives or halogenated groups that cause toxic by-products. Elements such as P, N and Si possess char forming ability that is an inherent part of many macromolecular system which can be exploited usefully in degradation chemistry.

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